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In-situ Raman monitoring of [2+2] cycloaddition of pyridine substituted olefins induced by visible laser

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Visible laser induced [2+2] cycloaddition of solid-state pyridine substituted olefins into cyclobutane has been monitored by an *in-situ* Raman technique. The laser power and wavelength can dramatically alter the reaction kinetics, as a prior melting process (heating from laser irradiation) is required for this [2+2] photoreaction.

Cyclobutanes constitute the backbone of many natural products and pharmaceutically and biologically interesting molecules, which can also act as reactive, intermediates for further ring-opening and ring expansion reactions.[1-3] [2+2] photodimerization of olefins into cyclobutanes has been widely studied for its ease in controlling the reactions and high conversion rates.[4] Typically, UV light is applied as the light source to initialize the [2+2] photoreactions, and solid-state nuclear magnetic resonance (NMR) and X-ray diffraction (XRD) techniques are used to characterize the reaction products.[5-7] For instance, a recent study demonstrated a single crystals popping phenomenon under UV light, which actually derives from a photosalient effect triggered by a [2+2] cycloaddition reaction.[8]

Besides UV triggered reactions, laser induced chemical reactions has attracted more and more attention,[9-11] including coupling reactions,[12, 13] photodimerization,[14, 15] photochromic reactions.[16] Moreover, *in-situ* Raman spectroscopy is appealing for studying photoreactions in a way that the reactions can be induced by the laser source, and simultaneously, the reaction processes (bond formation) can be monitored by the variation of the Raman fingerprints.[17-19] Our previous works have also shown visible laser induced catalytic reactions,[20, 21] which utilizes the surface plasmon generated at metal surface to initialize the chemical reactions. Herein, we demonstrate an *in-situ* Raman monitoring of visible laser induced [2+2] cycloaddition of solid-state pyridine substituted olefins (Scheme 1), where crystals of pyridine substituted olefins are formed using different silver complexes. Disappearance of C=C double bonds and formation of cyclobutanes can be easily captured from the time-dependent Raman spectra. Notably, laser power- and wavelength-dependent reaction rates of this [2+2] photoreaction have been

distinguished, and melting point of the formed crystals can also influence the reaction process. We believe this study may open up new avenues for studying photo-induced chemical reactions.

Crystals of pyridine substituted olefins were synthesized through a crystal engineering method, where silver salts were used to induce the crystallization of the one end capped pyridine substituted olefins (see Experimental Section in ESI for detail†).[22] Here, crystals of $[Ag_2(4\text{-}VP)_4][TFA]_2$ (**1**) (4-VP = 4-vinylpyridine, TFA = trifluoroacetate) and $[Ag_2(PEA)_4][TFA]_2$ (PEA = Ethyl-(pyridine-4-yl)prop-2-enoate) (**2**) were prepared for the study of laser induced [2+2] cycloaddition. For comparison, cocrystal of $(BPE)_2 (RES)_2$ (BPE = *trans*-1,2-bis(4-pyridyl)-ethylene, RES = resorcinol) (**3**) and $(BPEP)_2 (RES)_2$ (BPEP = 1,3-bis(*trans*-4-pyridylethylenyl)pyridine) (**4**) were also prepared for laser induced [2+2] cycloaddition, where hydrogen bond formation leads to rigid supermolecular structure with high melting point of these two crystals.
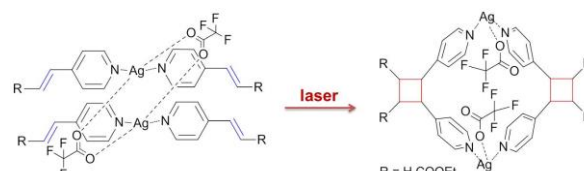
Scheme 1 Schematic illustration of [2+2] cycloaddition of pyridine substituted olefin crystal **1** and **2** induced by visible laser irradiation.

The as-prepared solid-state crystals of pyridine substituted olefins were placed under laser irradiation on a Renishaw In Via confocal Raman system, where *in-situ* Raman spectra were taken during the reaction process. Here, Raman line mapping was carried out over the crystal surface using a 633 nm laser at different powers (Fig. 1a). As shown in Fig. 1b, Raman spectrum of crystal **1** is characterized by the C=C double bond stretching at ~1633 cm^{-1}, pyridine ring stretching at ~1610 cm^{-1}, CH_2 deformation at ~1415 cm^{-1}, CH in-plane deformation at ~ 1204 cm^{-1}, pyridine ring breathing at ~1020 cm^{-1}, and CH in-plane bending at ~1065 cm^{-1}.[23] It has been found that [2+2] cycloaddition can be realized immediately under 100% (3

mW) laser power, confirmed by a typical Raman spectrum of crystal **1** after laser irradiation (Fig. 1b). The disappearance of the C=C fingerprint and emergence of the peak at ~1145 and 844 cm^{-1} corresponding to the cyclobutane skeletal C-C stretching mode and C(cyclobutane)-C(pyridine) stretching mode[23] verify that olefins have been completely converted into cyclobutane structures.
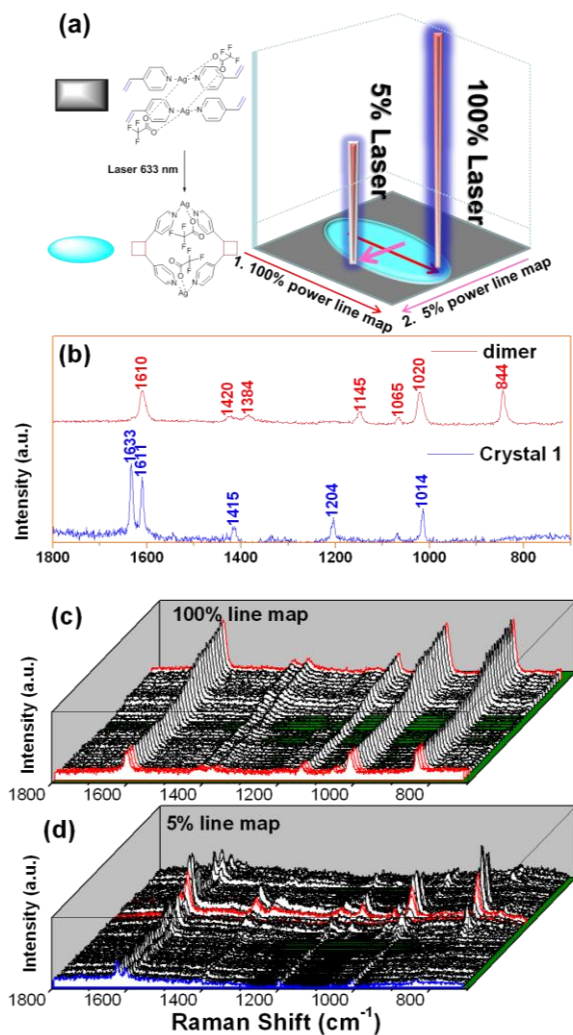
Fig. 1 (a) Schematic illustrations of Raman line maps on crystal **1**; (b) Raman spectra recorded from the unreacted area (blue line) and reaction centre (red line); (c) The collective diagram of Raman spectra line map with 100% (3 mW) laser power; (d) the collective diagram of Raman line map crossing the reacted area with 5% (0.15 mW) laser power. Laser: 633 nm.

The laser induced reaction can also be confirmed by the fact that the peak at 1415 cm^{-1} (CH$_2$ deformation) was split into two peaks at ~1420 and 1384 cm^{-1}.[24] Through the Raman line map using 100% (3 mW) laser power in Fig. 1c, one can see that the crystal surface exposed to the laser beam underwent rapid [2+2] cycloaddition photoreactions, leading to complete conversion of olefins into cyclobutanes. Notably, a laser power-dependent reaction feature was witnessed (Fig. 1d). When a Raman line map with 5% (0.15 mW) power was taken vertical to the previous one, such a power failed to induce the cycloaddition reaction in a short time, but one can easily find that photoreaction has been occurred in the irradiated part with 100% (3 mW) power (also see Fig. S1 in ESI†). However, a careful time-dependent study reveals that such reaction is laser power-dependent, and typically lower laser power consumes longer reaction time to discover the occurrence of the cycloaddition reaction (see Fig.

S2 in ESI†). This indicates that in our case, [2+2] cycloaddition of solid-state pyridine substituted olefins mainly arises from a heat effect of the applied laser. To further confirm the above results, control experiment using UV irradiation was carried out (see Fig. S3 in ESI†), which shows similar spectroscopic variations relating to the vanished C=C bonds and newly formed cyclobutanes.
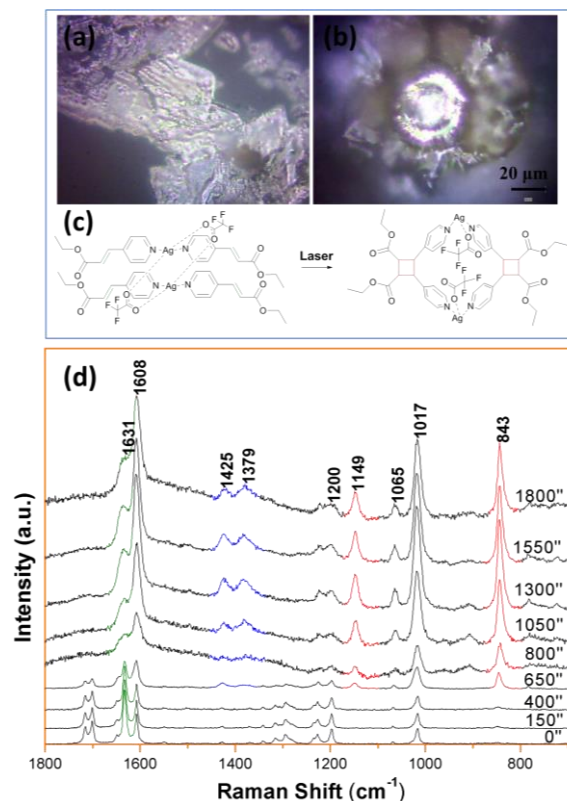
Fig. 2 Optical images of crystal **2** before (a) and after (b) laser irradiation; (c) Schematic illustration of crystal **2** undergoing [2+2] cycloaddition induced by laser irradiation; (d) The time-dependent Raman spectra showing the [2+2] dimerization process of crystal **2** with 50% (1.57 mW) power of 633 nm laser.

Crystal **2**, [Ag$_2$(PEA)$_4$][TFA]$_2$, can also undergo visible laser induced cycloaddition reaction, as shown in the time-depended Raman spectra recorded on the solid crystal (Fig. 2). PEA was synthesized and confirmed by ^{1}H and ^{13}C NMR spectra (see Fig. S4 and S5 in ESI†), and crystal information of **2** was determined (CCDC number: 1025966). It can be seen from the optical images that the crystal surface will be melted by the laser irradiation. The laser induced cycloaddition can be manifested by the vanishing 1631 cm^{-1} peak (C=C double bond stretching), and the appearing peaks at ~1149 and 843 cm^{-1} corresponding to the skeletal C-C stretching of cyclobutane and C(cyclobutane)-C(pyridine) stretching mode, respectively.[23] The split weak peaks at 1425 and 1379 cm^{-1} can be assigned to the CH$_2$ deformation cyclobutane. The disappearance of carboxyethyl (-COOEt) at ~1701 and 1716 cm^{-1} (Fig. 2d) is caused by disorder during cyclobutane formation.[25] The slight peak shift for the C=C and cyclobutane groups found for crystal **1** and **2** results from the different substituting group at the end of the olefins. Nevertheless, it has been verified that visible laser induced cyclobutane formation does occur on these two solid state pyridine substituted olefins. However, we have noticed that the exactly same pyridine substituted olefins in liquid state cannot be converted into cyclobutanes when identical laser irradiation is applied. In fact, [2+2] photodimerization that can be completed in liquid phase normally applies UV light or UV laser, and the presence of proton acid as

template is also required.[26, 27] With visible laser source, some successful examples have been reported in liquid/ solid state.[14] So, it comes to conclusion that silver or proton ion as template is essential for the cycloaddition reaction in solid/ liquid.

In addition to the laser power, applied laser wavelength can also greatly alter the reaction kinetics of this [2+2] cycloaddition. Using a similar power (1.18 mW) of 532 nm laser, *v.s.* 1.65 mW of 622 nm laser, it turns out that the reaction rate of the [2+2] dimerization (crystal **1** and **2**) is much faster (see Fig. S6 in ESI†). Moreover, carbonization of the formed crystals can be seen under an even higher power of 532 nm laser (6.35 mW), as we can clearly distinguish the D and G bands of carbon materials (see Fig. S7 in ESI†). It needs to be pointed out that reaction under 532 nm laser would be too fast to capture the spectroscopic evolution for this [2+2] photoreaction, and thus here 633 nm laser is typically applied. We believe this reaction rate variation under lasers of different wavelengths results from a more efficient and rapid heating effect on the crystals with shorter wavelength lasers.

It is important to note that when cocrystals **3** and **4** were used as pyridine substituted olefins to study the laser induced cycloaddition, no changes in the Raman spectra can be distinguished even with 100% (3 mW) power of 633 nm laser (see Fig. S8 and S9 in ESI†). From the optical images, one can see that cocrystals **3** and **4** cannot be melted under laser irradiation. Therefore, we think the melting process is necessary to trigger the cycloaddition reaction. The hydrogen bonds formed in the rigid supermolecular cocrystal structures give melting points of 225 and 211 °C for crystals **3** and **4**. While the crystals formed with silver salts have much lower melting points, 64.5 °C for crystal **1** and 66 °C for crystal **2**. Besides the topochemical considerations (one end capped with H/COOEt can give the double bonds more freedom to move/ dimerize[28]), the melting point can be regarded as a criterion to evaluate the photoreactivity of pyridine substituted olefins under laser irradiation.

In conclusion, visible laser induced [2+2] photodimerization of solid state pyridine substituted olefins has been studied. The formation of cyclobutane and disappearance of the vinyl group can be easily monitored from the *in situ* Raman spectra. It has been found that the laser induced cycloaddition reaction is laser power- and wavelength-dependent, and the topochemistry and melting point of the crystals can determine the reactivity of such reactions. Crystals formed by TFA cation complexation can undergo [2+2] cycloaddition reactions, while those formed by hydrogen bonds with higher melting point cannot. Compared to UV induced [2+2] photodimerization reactions, this laser induced reaction process on a Raman platform offers a new avenue to study photochemical reactions due to the possibility of simultaneously inducing and monitoring the reactions.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental, Fig. S1-S9, CIF for Crystal **2** and **4**. See DOI: 10.1039/c000000x/

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